

# Comparison of the Adsorption of Carbofuran at the Silica–Liquid and Liquid–Vapour Interfaces

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**Abstract:** The adsorption processes of carbofuran from an aqueous solution have been determined at the solid–liquid interface, onto silica and at liquid–vapour interfaces. At the solid–liquid interface, the adsorption isotherms and their evolution with temperature reveal that adsorption is generally weak but increases with temperature. Adsorption also significantly increases with concentration when the solubility limit is approached. The study at the liquid–vapour interface reveals that adsorption at this interface is 70 times larger than at the solid–liquid interface. Again, adsorption values at the liquid–vapour interface increase with temperature (below 30°C) and near the solubility limit. Consequences of the observations on the behaviour of carbofuran in the environment are discussed.

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**Key words:** adsorption; surface tension; pesticide; solid–liquid interface; liquid–vapour interface; solubility; carbofuran

## 1 INTRODUCTION

The adsorption of carbofuran has been studied in many cases on different types of soil.<sup>1–5</sup> Recent work<sup>6</sup> in our laboratory confirmed that the adsorption of carbofuran on silica is small, but we have shown that this increases with temperature and near the solubility limit. This fact is worth underlining because the quantity of free water in soil is generally limited. This study has also shown that kinetics of solution are very slow in water and that desorption is possible. When pesticides are adsorbed on solids, they often, but not always, retain their physical and chemical properties,<sup>7</sup> so, when they are desorbed, they are active. Most pesticides are to some degree toxic to animals and mammals and their degradation could be very slow depending on the type of soil. For instance, Szeto and Price<sup>8</sup> reported persistence of carbofuran and fensulfothion at the concentrations of 78 and 92  $\mu\text{g g}^{-1}$ , respectively, in Fraser Delta silt loam soils, where the pH values of soils were between 5.0 and 5.9,<sup>9</sup> almost a year after labelled granular application. Other per-

sistance phenomena occur in which soils must play only an indirect role. A recent study on pesticides has revealed a high concentration of pesticides in rain-water.<sup>10–13</sup>

That is why we considered it necessary to know what phenomena would be able to take place at the liquid–vapour interface. We therefore estimated the adsorption of carbofuran at the liquid–vapour interface from surface tension measurements and compared this with the relative adsorption values at the solid–liquid interface, because the presence of pesticides in water may arise from their desorption from solid surfaces.

## 2 THEORETICAL

### 2.1 Adsorption at the solid–liquid interface

Usually, adsorption at the solid–liquid interface is calculated as

$$Q_{\text{ads}} = (C_0 - C_e) \frac{V}{m} \quad (1)$$

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with  $C_0$  the initial concentration of the volume  $V$  of solution agitated with mass  $m$  of silica.  $C_e$  is the concentration of the supernatant isolated from silica by centrifugation after equilibrium.

In the present work, adsorption at the solid-liquid interface was calculated as the relative adsorption, according to Gibbs,  $\Gamma_{2,1}$  in  $\text{mol cm}^{-2}$ . The suffix 2 represents the solute (carbofuran) and the suffix 1, the solvent (water). If  $n^0$  is the total number of moles in the sample,  $x_2^0$  is the initial mole ratio of carbofuran, and  $x_2$  the equilibrium mole ratio of the supernatant after adsorption,

$$\Gamma_{2,1} = \frac{1}{x_1} \frac{n^0(x_2^0 - x_2)}{mS} \quad (2)$$

with  $S$  the specific area of silica,  $m$  the mass of silica and  $x_1$  the mole fraction of water in the supernatant.

$\Gamma_{2,1}$  is independent of the total surface of solid, since it is given for  $1 \text{ cm}^2$ , and is a significant thermodynamical parameter, useful, for instance, in calculations of temperature effects on adsorption, or in calculations of surface tensions at the solid-liquid interface. In most experiments on soils, it is impossible to calculate  $\Gamma_{2,1}$  since the solid component is not homogeneous and even the mean specific area of the solid is unknown. In the present case, adsorption was calculated as  $Q_{\text{ads}}$  in micrograms of carbofuran adsorbed per gram of silica powder, but in very dilute solutions, it is easy to show that

$$\Gamma_{2,1} \approx \frac{Q_{\text{ads}}}{M_2 S} \quad (3)$$

where  $M_2$  is the molar weight for component 2.<sup>6</sup>

## 2.2 Adsorption at the liquid-vapour interface

The relative adsorption values at the liquid-vapour interface can be calculated from surface tension values through Gibbs' equation.

$$\Gamma_{2,1} = -\frac{1}{RT} \left[ \frac{\partial \gamma}{\partial \ln a_2} \right]_T = -\frac{a_2}{RT} \left[ \frac{\partial \gamma}{\partial a_2} \right]_T \quad (4)$$

where  $\gamma$  is the surface tension in  $\text{mN m}^{-1}$ ,  $R$  the gas constant in  $\text{J K}^{-1} \text{mol}^{-1}$ ,  $T$  the temperature in K and  $a_2$  the activity of carbofuran.

In dilute solutions,  $a_2 = c_2$ , so  $\ln a_2 = \ln c_2$ , where  $c_2$  is the concentration of solute ( $\text{mol litre}^{-1}$ ) so that

$$\Gamma_{2,1} = -\frac{c_2}{RT} \left[ \frac{\partial \gamma}{\partial c_2} \right]_T \quad (5)$$

## 3 MATERIALS AND METHODS

### 3.1 Chemicals

Carbofuran, certified for laboratory use, 99.9% pure, was supplied by Dr. Ehrenstorfer, GmbH. Water was purified on a Millipore Q filtration system. Silica was Aerosil 200, a pyrogenic silica of specific area  $200 \text{ m}^2 \text{g}^{-1}$  was supplied by Degussa.

### 3.2 Experimental method

For the determination of adsorption at the solid-solution interface the classical gravimetric method was used,<sup>1,2,14,15</sup> in accordance with the methodology described by Mear *et al.*<sup>6,16</sup>

Samples of silica powder (0.4 g) were weighed into centrifuge tubes, and 10 g of aqueous solutions of carbofuran were added and agitated during the time necessary to obtain equilibrium. This time has been previously measured by adsorption kinetics experiments as described below. During agitation, the samples were kept in a thermoregulated oven.

Adsorption was then determined by removing the silica powder from the suspensions by centrifugation at  $2000g$  in a FirLabo for 3 h and titration of the supernatant by UV spectrometry on a UVIKON 930 spectrophotometer, at a wavelength of 276 nm which corresponds with a peak on the spectrum. One-centimetre cuvettes were used. The slope of the calibration line was found to be  $213.7 (\pm 0.3) \text{ litre mol}^{-1}$ , so a precision of 0.1% was expected for  $x_2$  values.  $\Gamma_{2,1}$  was calculated through eqn (2).

Surface tensions were measured with a Lauda TC1 tensiometer and the classical ring method,<sup>17,18</sup> using a platinum ring perfectly wetted by the solutions. All glassware and the platinum ring were treated with a sulfochromic mixture and rinsed with water filtered on the milliQ system to avoid pollution by surface-active substances. The tensiometer was kept in a thermostat, and all solutions were placed in a water-thermoregulated cell so as to minimize the temperature gradient at the liquid-vapour interface.

Since solutions were very dilute, surface tension variations were small and particular care had to be taken for precision; all corrections for the ring used were made.<sup>19</sup>

Adsorption at the liquid-vapour interface was calculated through eqn (5).

## 4 RESULTS AND DISCUSSION

### 4.1 Adsorption at the solid-liquid interface

The study was made at 35, 30, 25, 20, 15 and  $10^\circ\text{C}$ . An example of the adsorption isotherm (Fig. 1) shows it to

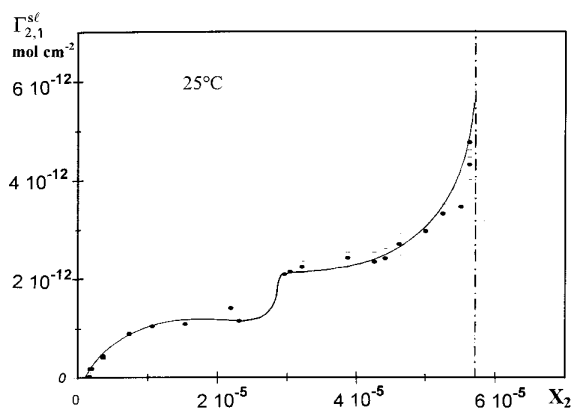


Fig. 1. Adsorption isotherm of carbofuran from water on silica at 25°C. The vertical line indicates the solubility limit.

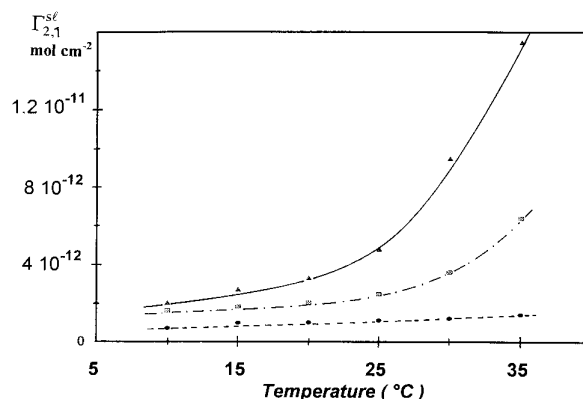


Fig. 2. Evolution of adsorption values at the solid-liquid interface, versus temperature for the two plateaux and at the solubility limit. (-----) first plateau, (-·-·-·-) second plateau, (—) maximal adsorption (at the solubility limit).

be of the S4-type with respect to the Giles classification.<sup>20</sup> Consequently, the interactions between solute and surface are weak, but interactions between solute and solvent induce the adsorption of carbofuran on silica.<sup>21</sup> These interactions are obviously strong, because carbofuran solubility is very low,<sup>6</sup> and they are able to expel carbofuran molecules from solution. Two plateaux characterize the isotherm. Plateaux are not commonly observed in adsorption isotherms, successive plateaux are still less common. The usual explanation for a plateau is the geometrical saturation of the surface by the solute molecules, as in Langmuir's isotherms.<sup>20–22</sup> According to the adsorption value on the plateau, any full saturation of the surface is obtained; for flat molecules, whose area is about 42 Å, one should obtain about  $3.95 \times 10^{-10} \text{ mol cm}^{-2}$ . However another saturation type can be considered: a first dilute layer can be formed on a given type of site on the silica. After saturation of these sites, adsorption remains constant until other sites become more active, or another layer forms on the first one. What is sometimes observed with big molecules, such as polymers, is a change in the conformation of the adsorbed molecules, and/or an orientation change, which allows adsorption of further quantities of solute.<sup>16,20,21</sup> Each of these possibilities can be considered for carbofuran adsorption, but complementary techniques such as ellipsometry or surface spectroscopy are necessary to give a correct idea of reality.

Figure 2 shows the evolution of the two plateaux and the adsorption at the solubility limit versus temperature. It can be seen that the first plateau does not greatly change with temperature, but the second plateau is influenced by it, so we can conclude that molecules adsorbed on the second plateau are sensitive to thermal fluctuations and consequently are less strongly linked to the surface. This has also been seen in a desorption experiment. (Mear, A.-M., Le Gall, A., Privat, M., unpublished results.)

Near the solubility limit, the adsorption increases with temperature, particularly above 25°C.

In our system the surface favours carbofuran-carbofuran interactions and consequently the nucleation of carbofuran crystals which appear when bulk demixing occurs and adsorption will be stronger when approaching demixing.

The strong adsorption near the solubility limit is now classical. Theory<sup>23</sup> and experimental results<sup>24</sup> show that, close to a bulk phase change, local concentration fluctuations occur: short-time clusters having the new phase concentration appear. In statistical thermodynamics this is expressed through molecule correlation functions characterized by correlation lengths, which are the cluster diameters. Close to demixing it is also shown that the adsorption layer thickness is proportional to the correlation length due to the new phase nucleation process. It is well known that new phases preferentially form in parts of systems where an inhomogeneity occurs, as in surfaces.

#### 4.2 Adsorption at the liquid-vapour interface

Surface tension measurements were made at 35, 25, 15, 10 and 5°C on all the possible concentration ranges. At 40, 30 and 20°C, only concentrations near the solubility limit were studied. Surface tensions are represented in Fig. 3 versus the reduced concentration,  $c_2/c_{co}$ , where  $c_2$  is the molar concentration of carbofuran and  $c_{co}$  is the concentration of carbofuran at the solubility limit.

It can be seen that, below 35°C, the value of the surface tension decreases when the concentration and the temperature increase. At 35°C, a plateau appears near to the demixing point. At 40°C, measured surface tensions close to demixing also show a plateau whose value is slightly larger than at 40°C ( $60.5 \text{ mN m}^{-1}$  instead of  $58 \text{ mN m}^{-1}$ ).

From the surface tension values, using Gibbs' equation, the relative adsorption at the liquid-vapour interface was calculated and results are shown in Fig. 4. Adsorptions at the solubility limit have been determined using an extrapolation method and are shown in

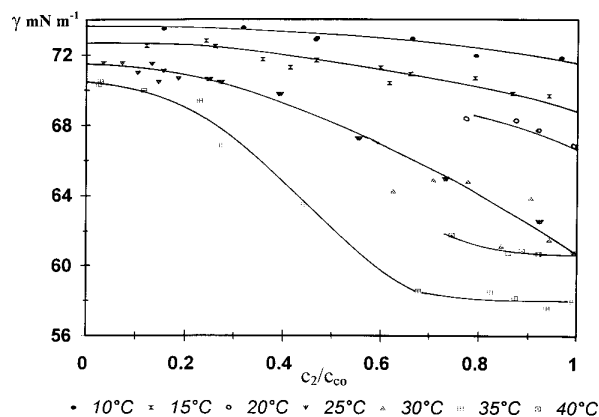


Fig. 3. Surface tension of carbofuran solutions at the liquid-vapour interface, at different temperatures, versus the reduced concentration,  $c_2/c_{\infty}$ .

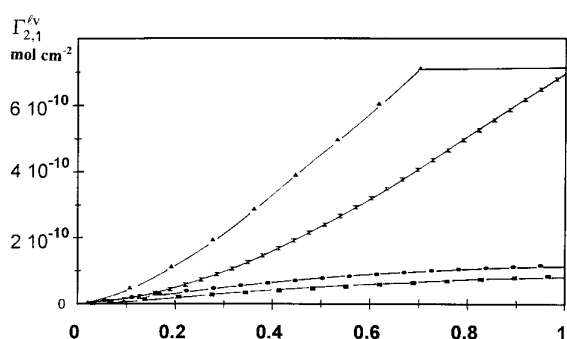


Fig. 4. Relative adsorption of carbofuran at the liquid-vapour interface in  $\text{mol cm}^{-2}$ , versus reduced concentration  $c_2/c_{\infty}$  at (■) 10, (●) 15, (×) 25 and (▲) 35°C.

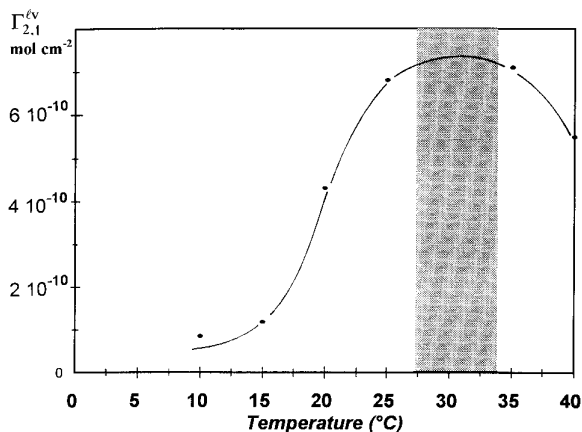


Fig. 5. Relative adsorption at the liquid-vapour interface at the solubility limit versus temperature.

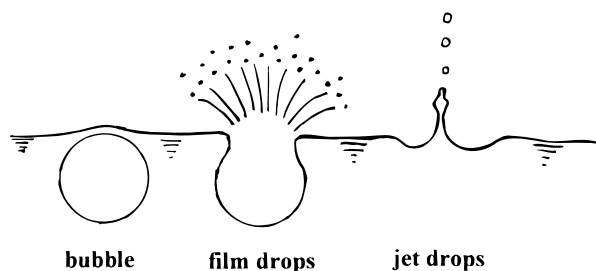


Fig. 6. Schematic representation of the production of film drops and jet drops by bubble bursting.

Fig. 5. It can be seen that the relative adsorption first increases then decreases, with a maximum near 30°C.

#### 4.3 Comparison of the relative adsorption at the two interfaces near the demixing point

If we compare values of the adsorption at the two interfaces near the demixing point, Figs 2 and 5, we can see that the adsorption at the liquid-vapour interface is 70 times larger than at the solid-liquid interface.

Although the leading phenomenon for adsorption was the water-carbofuran interaction, interactions between silica and water, and between silica and carbofuran play a role. Obviously water keeps its strong affinity for silica even in the mixture, while carbofuran behaves more as a hydrophobic component. Against air, which must be considered as hydrophobic, carbofuran adsorption must be far stronger, as is observed.

These results are very important to predict what becomes of carbofuran in nature. Adsorption on soils contributes to fixing carbofuran, but it is also a water-pollution source. Adsorption at the water surface is very large. This means that there is a high possibility of it passing into the atmosphere. There are at least two ways for organic molecules to pass into the atmosphere. The first one is an equilibrium phenomenon: as the chemical potential of organic molecules must be the same in water and in vapour at thermodynamic equilibrium, molecules pass into the atmosphere until the vapour pressure is reached. As the system is open, equilibrium is rarely reached, and there is always an organic entry into the atmosphere. The phenomenon is the same as for gases dissolved in water.<sup>25</sup> If molecules have a high affinity with the surface, this entry is favoured; the final value of the vapour pressure is, of course, not altered, but equilibrium can be reached faster. The second cause is a dynamic one. Wind stirring the water surface generates small drops, forming three types of aerosol: sea spray, film drops and jet drops.<sup>26</sup> Spray forms from 'tearing' and/or wave breaking; film drops and jet drops forms from air bubbles bursting at the surface (Fig. 6); bubbles are entrained in water during wavebreaking, then rise to the surface and burst. It is easy to understand that an aerosol formed from a carbofuran-rich surface layer must also be carbofuran-rich. Aerosol driven by winds can carry the pesticide long distances.

## 5 CONCLUSION

This work has shown that the adsorption at the liquid-vapour interface was 70 times larger than at the solid-liquid interface. After the solution of carbofuran, or after desorption,<sup>6</sup> molecules present in solution can accumulate at the water surface and, by dispersion by wind, could pass in the atmosphere. This work shows

that it is important to compare the two interfaces, i.e. solid-liquid and liquid-vapour, in order to follow the evolution of pesticides in the environment. Despite confining this study to silica, and to only one pesticide, results could give indications for other pesticide studies. It would be interesting to continue this type of study with the degradation products of pesticides, or with other pesticides.

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